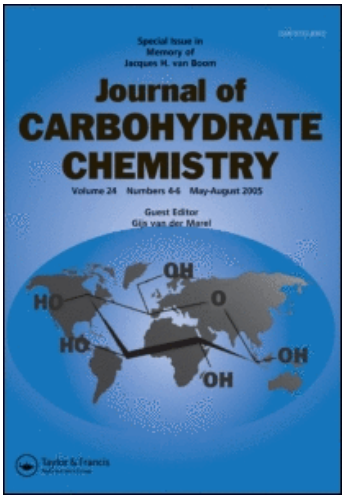

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Brzezinska, Ewa and Michalska, Maria(1990) 'Studies on the Reaction of Sugar Aziridines with Organophosphorus Acids. Regio- And Stereo-Selective Ring-Opening of Methyl 4, 6-0-Benzylidene-2, 3-Dideoxy-2, 3-Epimino-α-D-Manno-and Allopyranosides with 0,0-Dialkylphosphorodithioic Acids', Journal of Carbohydrate Chemistry, 9: 4, 451 — 460
To link to this Article: DOI: 10.1080/07328309008543845
URL: http://dx.doi.org/10.1080/07328309008543845

J. CARBOHYDRATE CHEMISTRY, 9(4), 451-460 (1990)

STUDIES ON THE REACTION OF SUGAR AZIRIDINES WITH ORGANOPHOSPHORUS ACIDS. REGIO- AND STEREO-SELECTIVE RING-OPENING OF METHYL 4,6-O-BENZYLIDENE-2,3-DIDEOXY-2,3-EPIMINO-α-D-MANNO-AND ALLOPYRANOSIDES WITH O,O-DIALKYLPHOSPHORODITHIOIC ACIDS

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Received July 9, 1989 - Final Form March 2, 1990

ABSTRACT

Ring-opening reactions of methyl 2,3-N-acetylepimino-4,6-O-benzylidene-2,3-dideoxy-α-D-mannopyranoside (2) and-α-D-allopyranoside (4) with phosphorodithioic acids 5 and 6 proceed smoothly at ambient temperature to give exclusively products of altro configuration in quantitative yields. A similar stereoselective reaction between methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino-α-D-mannopyranoside (1 and -α-D-allopyranoside (3) and the alkylammonium salt of the acid 6 requires more vigorous conditions.

INTRODUCTION

Aziridines represent a very reactive class of compounds which, due to the presence of a strained three-membered ring and of the ring nitrogen may undergo a variety of reactions. The lone electron pair on the nitrogen atom causes a close resemblance of this class of compounds to non-aromatic amines and as such, aziridines may undergo reactions with preservation of the three-membered ring. The aziridine ring strain, on

the other hand, facilitates reactions which lead to ring-opening and consequently, to the introduction of a large variety of nucleophiles in addition to the amino functionality thus formed. Activated acyl aziridines easily undergo nucleophilic ring-opening due to the presence of a nitrogen substituent capable of stabilizing the negative charge which is formed on the aziridine nitrogen in the transition state when the compound reacts with a nucleophile.[1]

Basic aziridines are less prone to ring-opening than their N-acetyl derivatives, and accordingly, ring opening requires more drastic conditions.

The reactions of simple epimines with phosphoric,[2] phosphoroselenoic[3] and phosphorodithioic acids[4,5,6] were the subject of considerable interest. Christensen[2] performed the ring-opening of ethylenimine with phosphoric acid in order to synthesize esters related to naturally occuring phosphatides. Later Akerfeldt and Fagerlind[3] found that phosphoroselenoic acids react readily with ethylenimine and other aziridines to give potent inhibitors of cholinesterase. The patent literature[4,5,6] reports on insectisides, herbicides and acaricides obtained by reaction of ethylenimine with dialkylphosphorodithioic acids.

The interest in sugar aziridines arose in connection with the synthesis of antiradiation[7] and anticancer[8,9] drugs, dideoxy aminosugars[10] and aminosugar antibiotics.[11]

The ring-opening reaction of sugar aziridines has not thus far been employed as a route towards the synthesis of carbohydrates containing vicinal amino and thiophosphoryl functions. This task was undertaken in our laboratory[12] in extension of our studies on epoxide ring-opening with phosphorus-sulphur nucleophiles.[13,14]

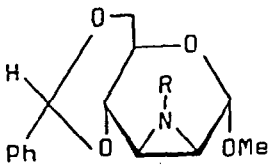
RESULTS AND DISCUSSION

We chose two basic and two activated N-acyl aziridines for our investigations: methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino-α-D-mannopyranoside (1)[15] and its N-acetyl derivative 2, and methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allopyranoside (3)[15,16] and its N-acetyl derivative 4. The organophosphorus acids employed in epimine ring-

opening reactions were: 5,5-dimethyl-2-mercapto-2-thiono-1,3-dioxa-2-phosphorinane (5)[17] and O,O-dineopentylphosphorodithioic acid (6).[18]

The reactions of N-acetylepimine 2 and 4 with O,O-dialkylphosphorodithioic acids 5 and 6 were performed in chloroform solutions at ambient temperature. When methyl 2,3-N-acetylepimino-4,6-O-benzylidene-2,3-dideoxy-α-D-mannopyranoside (2) was allowed to react with 5,5-dimethyl-2-mercapto-2-thiono-1,3-dioxa-2-phosphorinane (5), the reaction was accomplished within 24 h (^{31}P NMR). According to ^{31}P NMR one phosphorus-containing product was formed, and at quantitative yield. The trans-diaxial structure of the isolated methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-S-(5',5'-dimethyl-2'-thiono-1',3'-dioxa-2'-phosphorinanyl)-3-thio-α-D-altropyranoside (7) was confirmed by the low $J_{1,2}$ value (<1 Hz) which proved the eq-eq (trans) arrangement of H-1 and H-2. When the reaction of 2 with the acid 5 was performed in the presence of stoichiometric amounts of water, debenzylidenation occurred following the addition process. Methyl 2-acetamido-2-deoxy-2-S-(5',5'-dimethyl-2'-thiono-1',3'-dioxa-2'-phosphorinanyl)-3-thio-α-D-altropyranoside (8), sparingly soluble in chloroform, precipitated from the reaction mixture. The steric course of the ring-opening reaction is in agreement with the observations of Buss, Hough and Richardson[10] and is analogous to that established in our earlier work on 2,3-manno-epoxide ring-opening with O,O-dialkylphosphorodithioic acids.[14] The reaction of the epimine 2 with O,O-dineopentylphosphorodithioic acid (6) proceeded according to the same pattern. Its rate was considerably slower due to the steric requirements of the two neopentyl groups. The reaction performed at ambient temperature was completed within 5 days. Also in this case only one product (9), was formed in quantitative yield, to which the trans-diaxial structure was ascribed on the basis of a value of $J_{1,2}$ coupling constant lower than 1 Hz.

The reaction between the N-acetyl-allo-epimine 4 and phosphorodithioic acid 5 was performed under similar conditions and was accomplished within 24 h yielding the 2-substituted methyl 3-acetamido-4,6-O-benzylidene-3-deoxy-2-S-(5',5'-dimethyl-2'-thiono-1',3'-dioxa-2'-phosphorinanyl)-2-thio-α-D-altropyranoside (10) as the only product and in quantitative yield.



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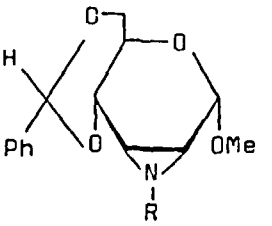
2 R = Ac



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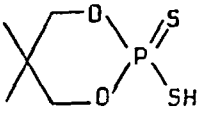
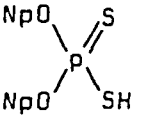
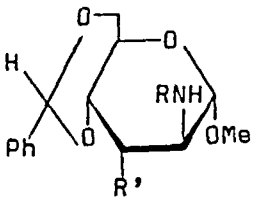
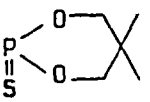


5

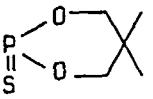


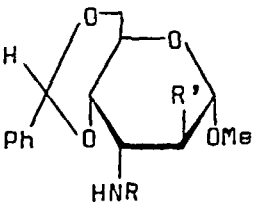
6 Np = $-CH_2C(CH_3)_3$



7 R = Ac
R' = 

9 R = Ac
R' = $-SP(ONp)_2$
S

12 R = H
R' = 



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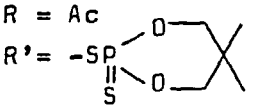
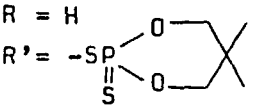
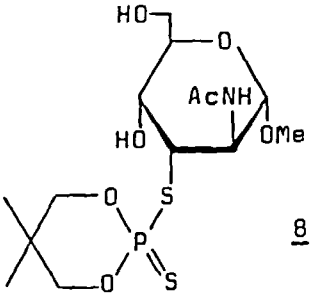
R' = 

11 R = Ac
R' = $-SP(ONp)_2$
S

13 R = H
R' = 



8

When the allo-epimine 4 reacted with phosphorodithioic acid 6 the reaction was slow at ambient temperature (7 days) but quantitative and fully regio- and stereoselective, yielding methyl 3-acetamido-4,6-O-benzylidene-3-deoxy-2-S-(dineopentyloxyphosphinothioyl)-2-thio-α-D-altropyranoside (11). The H-1 and H-2 arrangement in both 10 and 11 was confirmed by the presence of a narrow doublet signal for H-1 with a $J_{1,2}$ coupling constant = ~1 Hz. These two reactions took a different course from that described in our earlier work on allo-epoxide ring-opening with phosphorodithioic acids.[14] The reaction between methyl 2,3-anhydro-4,6-O-benzylidene-α-D-allo-pyranoside and the acid 5 was not regio- and stereoselective and gave two products: the diaxial and the diequatorial, in 2:1 ratio, respectively.

As mentioned before, nucleophilic ring-opening of free epimines requires more vigorous conditions. The reaction of epimines 1 and 3 with free acids 5 and 6, performed in DMF solution at 100 °C lead to a complex mixture of products. However, ring-opening of the basic epimines, 1 and 3, was successfully performed by heating the epimines with the triethylammonium salt of the thermally more stable acid 6, in DMF solution, at 80-100 °C, for several hours. Under these conditions both epimines, 1 and 3, afforded trans-diaxial adducts 12 and 13, respectively. The altro configuration of 12 and 13, established by spectroscopic data, was additionally confirmed by N-acetylation leading to compounds which were identical with the previously obtained adducts 9 and 11, of trans-diaxial structure.

It is of interest to compare our results with those reported by other authors. We would like to emphasize that in all experiments described in these investigations only diaxial products were formed. Although this is the generally preferred steric course of aziridine ring-opening by nucleophilic reagents, diequatorial ring-opening is quite substantial in some cases[20,21] and, accordingly, mixtures of altro and gluco isomers are obtained. In a single case exclusive diequatorial ring-opening was observed.[19]

Thus, we achieved a convenient, fully regio- and stereoselective synthesis of aminosugars bearing the dithiophosphate group in the vicinal position to the amino function.

EXPERIMENTAL

General procedures. Melting points were determined with Boetius PHMK 05 apparatus and are uncorrected. Specific rotations were recorded at 20 °C using a Polamat A polarimeter. IR spectra were recorded with a Unicam SP-200G spectrometer. ^{1}H NMR spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a VARIAN 60 MHz spectrometer. ^{31}P NMR spectra were determined in $CDCl_3$ with H_3PO_4 as standard (JEOL 60 Mz FT operating at 24.3 MHz and BRUKER 300 Mz FT operating at 36.43 MHz). Elemental analyses were performed by Microanalytical Laboratory of the Centre Molecular and Macromolecular Studies of the Polish Academy of Sciences, Lodz. The progress of all reactions was monitored by ^{31}P NMR spectroscopy and by TLC. TLC was performed on aluminium sheets coated with Silica Gel 60 (F-254, E. Merck) to a thickness of 0.2 mm. Benzene-chloroform-acetone system 3:1:1 was used as eluent. Detection was effected by exposure to iodine vapours. Preparative chromatography on Silica Gel (E. Merck 0.2-0.5 mm) was performed with a mixture of hexane-chloroform.

Methyl 2-Acetamido-4,6-O-benzylidene-2-deoxy-3-S-(5',5'-dimethyl-2'-thiono-1',3'-dioxa-2'-phosphorinanyl)-3-thio-α-D-altropyranoside (7). To a solution of compound 2[15] (0.305 g, 1.0 mmol) in dry chloroform (15 mL) was added 5,5-dimethyl-2-mercapto-2-thiono-1,3-dioxa-2-phosphorinane[18] (5, 0.198 g, 1.0 mmol). The mixture was stirred at room temperature for 24 h, then concentrated and the residue crystallized (chloroform/diethyl ether) to give 7 (0.42 g, 83%) as colourless crystals, mp 201-202 °C, $[\alpha]_{578}^{20}$ +78 (c 0.7, $CHCl_3$); IR (KBr) 3360 (NH), 1680 and 1510 (amide), and 680 cm^{-1} (P=S); ^{31}P NMR δ 90.0; ^{1}H NMR δ 0.67 (s, 3H, -CMe), 1.10 (s, 3H, -CMe), 2.05 (s, 3H, NAc), 3.40 (s, 3H, MeO), 4.55 (d, 1H, $J_{1,2}$ < 1 Hz, H-1), 5.65 (s, 1H, -CHPh), 6.10 (bd, 1H, $J_{2,NH}$=10 Hz, NH), 7.1-7.6 (m, 5H, Ph).

Anal. Calcd for $C_{21}H_{30}O_7NPS_2$: C, 50.08; H, 6.02; N, 2.78. Found: C, 49.87; H, 6.10; N, 2.56.

Methyl 2-Acetamido-2-deoxy-3-S-(5',5'-dimethyl-2'-thiono-1',3'-dioxa-2'-phosphorinanyl)-3-thio-α-D-altropyranoside (8). N-Acetyl epiminomannopyranoside 2 (0.305 g, 1.0 mmol) was dissolved in chloroform (15 mL),

then acid 5 (0.198 g, 1.0 mmol) followed by an equimolar amount of water was added and the mixture stirred at room temperature. After 15 min a colourless crystalline product began to precipitate. After 4 h the precipitate was filtered off and washed with diethyl ether. It consisted of pure compound 8, mp 165-166 °C (insoluble in $CHCl_3$ and MeOH, decomposes in DMSO). Yield: quantitative. IR (KBr) 3420 (OH), 3310 (NH), 1640 and 1550 (amide) and 690 cm^{-1} (P=S).

Anal. Calcd for $C_{14}H_{26}O_7NPS_2$: C, 40.47; H, 6.32; N, 3.37; P, 7.46; S, 15.43. Found: C, 40.52; H, 5.93; N, 3.41; P, 7.08; S, 15.07.

Methyl 2-Acetamido-4,6-O-benzylidene-2-deoxy-3-S-(dineopentyloxyphosphinothioyl)-3-thio-α-D-altropytanoside (9). To a solution of methyl 2,3-N-acetylepimino-4,5-O-benzylidene-2,3-dideoxy-α-D-mannopyranoside[15] 2 (0.61 g, 2.0 mmol) in dry chloroform (20 mL) was added O,O-dineopentylphosphorodithioic acid[17] 6 (0.54 g, 2.0 mmol). The mixture was kept for 5 days at room temperature, then concentrated to give a crystalline mass. Recrystallisation from chloroform-ether gave 9 in quantitative yield: mp 222-223 °C, $[\alpha]_{578}^{20}$ +41 (c 1.47, chloroform); IR (KBr) 3415 (NH), 1690 and 1500 (amide) and 675 cm^{-1} (P=S); ^{31}P NMR ($CDCl_3$) δ +95.3; ^1H NMR ($CDCl_3$) δ 0.80 [s, 18H, 2 x $-C(CH_3)_3$], 2.00 (s, 3H, AcN), 3.35 (s, 3H, MeO), 4.50 (d, 1H, $J_{1,2}$ < 1 Hz, H-1), 5.60 (s, 1H, PhCH), 5.90 (bd, 1H, $J_{2,NH}$=10 Hz, NH), 7.30-7.70 (m, 5H, Ph).

Anal. Calcd for $C_{26}H_{42}O_7NPS_2$: C, 54.23; H, 7.37; P, 5.38. Found: C, 54.30; H, 7.23; P, 5.15.

Methyl 3-Acetamido-4,6-O-benzylidene-3-deoxy-2 -S-(5',5'-dimethyl-2'-thiono-1',3'-dioxa-2'-phosphorinanyl)-2-thio-α-D-altropyranoside (10). To a solution of N-acetylepiminoallopyranoside 4 (0.305 g, 1 mmol) in dry chloroform (20 mL) acid 5 (0.198 g, 1.0 mmol) was added and the mixture stirred at room temperature. After 24 h the mixture was concentrated to afford crystalline 10. Recrystallisation from chloroform-ether gave pure 10 (0.368 g, 73%): mp 106-107 °C, $[\alpha]_{578}^{22}$ +20 (c 2.05, chloroform); IR (KBr) 3420 (NH), 1680 and 1520 (amide) and 680 cm^{-1} (P=S); ^{31}P NMR δ 84.4; ^1H NMR δ 0.90 (s, 3H, C-Me), 1.20 (s, 3H, C-Me), 2.00 (s, 3H, AcN), 3.45 (s, 3H, MeO), 4.95 (d, 1H, $J_{1,2}$ < 1 Hz, H-1), 5.60 (s, 1H, -CHPh), 6.60 (bd, 1H, $J_{3,NH}$=10 Hz), 7.30-7.40 (m, 5H, Ph).

Anal. Calcd for $C_{21}H_{30}O_7NPS_2$: C, 50.08; H, 6.02; N, 2.78. Found: C, 49.82; H, 5.92; N, 2.73.

Methyl 3-Acetamido-4,6-O-benzylidene-3-deoxy-2-S-(dineopentyloxyphosphinothioyl)-2-thio-α-D-altropyranoside (11). A solution of methyl 2,3-N-acetylepimino-4,6-O-benzylidene-2,3-dideoxy-α-D-allopyranoside 4[15,16] (0.61 g, 2.0 mmol) and of the acid 6 (0.54 g, 2.0 mmol) in dry chloroform (20 mL) was stirred at room temperature. After 7 days ^{31}P NMR showed the presence of a large amount of starting material. The mixture was then refluxed for an additional 15 h until the ^{31}P NMR signal corresponding to the acid 6 disappeared. ^{31}P NMR confirmed the formation of only one phosphorus-containing product. The mixture was concentrated to a syrup which was chromatographed on silica gel. The extracts were dried ($MgSO_4$) and concentrated to afford 11 as a syrup (0.969 g, 84%): $[\alpha]_{578}^{22}$ +26 (c 2.47, chloroform); IR (film) 3440 (NH), 1680 and 1520 (amide) and 685 cm^{-1} (P=S); ^{31}P NMR ($CDCl_3$) δ +91.1; ^{1}H NMR ($CDCl_3$) δ 1.00 [s, 18H, 2 x -C-(CH_3)$_3$], 2.00 (s, 3H, AcN), 3.40 (s, 3H, MeO), 4.80 (d, 1H, $J_{1,2}$ < 1 Hz, H-1), 5.60 (s, 1H, CHPh), 6.55 (bd, $J_{3,NH}$=10 Hz, NH), 7.30-7.50 (m, 5H, Ph).

Anal. Calcd for $C_{26}H_{42}O_7NPS_2$: C, 54.23; H, 7.37; N, 2.43. Found: C, 54.44; H, 7.59; N, 2.56.

Methyl 2-Amino-4,6-O-benzylidene-2-deoxy-3-S-(dineopenthyloxyphosphinothioyl)-3-thio-α-D-altropyranoside (12). To a solution of methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino-α-D-mannopyranoside[7] (1, 0.789 g, 3.0 mmol) in dry N,N-dimethylformamide (DMF, 25 mL) was added the triethylammonium salt of the acid 6 (1.113 g, 3.0 mmol) and the mixture was heated for 3 h at 90-100 °C. It was then cooled and concentrated under vacuum to give a crystalline residue. Recrystallisation from chloroform gave pure 12 (0.882, 56%): mp 197-198 °C, $[\alpha]_{578}^{23}$ +33 (c 0.97 chloroform); IR (KBr) 3380 (NH_2) and 675 cm^{-1} (P=S); ^{31}P NMR ($CDCl_3$) δ +94.4; ^{1}H NMR ($CDCl_3$) δ 0.80 [s, 18H, 2 x C(CH_3)$_3$], 1.70-2.00 (bs, 2H, NH_2), 3.40 (s, 3H, MeO), 4.53 (d, 1H, $J_{1,2}$ < 1 Hz, H-1); 5.60 (s, 1H, -CHPh), 7.30-7.70 (m, 5H, Ph).

Anal. Calcd for $C_{24}H_4O_6NPS_2$: C, 54.0; H, 7.56; N, 2.63. Found: C, 54.10; H, 7.52; N, 2.78.

Using a standard acetylation procedure, amine 12 gave a quantitative yield of the N-acetyl derivative which was identical with the product 9 described above.

Methyl 3-Amino-4,6-O-benzylidene-3-deoxy-2-S-(dineopentyloxyphosphinothioyl)-2-thio-α-D-altropyranoside (13). A solution of methyl 4,6-O-benzylidene-2,3-dideoxy-2,3-epimino-α-D-allopyranoside[15,16] 3 (0.789 g, 3.0 mmol) and the triethylammonium salt of the acid 6 (1.113 g, 3.0 mmol) in N,N-dimethylformamide (DMF, 25 mL) was heated for 3 h at 90-100 °C, and then concentrated under vacuum to give a syrup. Crystallisation from diethyl ether-petroleum ether afforded 13 (0.950 g, 59%): mp 124-125 °C, $[\alpha]_{578}^{22}$ +23 (c 2.0 chloroform); IR (KBr) 3400 (NH_2) and 675 cm^{-1} (P=S); ^{31}P NMR ($CDCl_3$) δ +91.1; ^{1}H NMR ($CDCl_3$) δ 1.00 [s, 18H, 2 x $C(CH_3)_3$], 1.90 (s, 2H, NH_2), 3.40 (s, 3H, MeO); 4.85 (d, 1H, $J_{1,2}$ < 1 Hz, H-1), 5.65 (s, 1H, -CHPh), 7.3-7.5 (m, 5H, Ph).

Anal. Calcd for $C_{24}H_{40}O_6NPS_2$: C, 54.00; H, 7.56; P, 5.80; S, 12.00. Found: C, 54.19; H, 7.53; P, 5.92; S, 11.76.

The amine 13 was acetylated using a standard procedure to give the N-acetyl derivative, identical with 11.

ACKNOWLEDGMENT

This work was supported by a grant-aid from the Polish Academy of Sciences, CPBP-01.13.

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SPECIAL FOOTNOTE

Publication of this work was delayed due to the manuscript being lost in the mail.